THE CHEMISTRY OF THE MOLTEN CARBONATE PROCESS FOR SO_2 REMOVAL FROM STACK GASES*

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INTRODUCTION

The Atomics International Molten Carbonate Process for removal of sulfur oxides from power plant stack gases has been under development since 1966. A 10 Mw pilot plant is now under construction. This paper describes the process chemistry. Brief descriptions of the pilot plant and of process economics are also given.

PROCESS DESCRIPTION

In the Molten Carbonate Process, a molten eutectic mixture of lithium, sodium, and potassium carbonates is used to scrub the power plant gas stream. The sulfur oxides in the gas stream react with the carbonates to form sulfites and sulfates, which remain dissolved in excess unreacted carbonate melt. The molten carbonate-sulfite-sulfate mixture is then treated to convert the sulfite and sulfate back to carbonate and to recover the sulfur as elemental sulfur. The regenerated carbonate is then recirculated to the scrubber to repeat the process cycle.

The regeneration of carbonate is done in two steps: 1) the reduction of the sulfite and sulfate to sulfide, and 2) the conversion of the sulfide to carbonate plus hydrogen sulfide. The reduction step is accomplished by reaction with a form of carbon, such as petroleum coke. The conversion of the sulfide to carbonate is accomplished by reacting the melt with steam and carbon dioxide, liberating hydrogen sulfide. The hydrogen sulfide is then converted to elemental sulfur in a Claus plant.

The process flow diagram is shown in Figure 1. The process steps are as follows:

1) The gas to be treated is removed from the boiler at about $450^{\circ}C$ and, if the boiler is burning coal, the gas passes through a high temperature, high efficiency electrostatic precipitator where essentially all the fly ash is removed. The gas then passes through the scrubber, where the sulfur oxides are removed by contacting the gas stream with a spray of molten carbonate at $450^{\circ}C$. This gas-liquid contact removes 95% or more of the sulfur oxides and most of the remaining ash from the gas stream. The cleaned gases are then returned to the boiler for further heat recovery, and eventually pass out the stack.

2) The molten salt stream containing carbonate (M_2CO_3, where M = the mixture of Na, K, and Li), sulfite (M_2SO_3), sulfate (M_2SO_4) and ash from the scrubber is pumped to a purification system and filtered to remove the ash. The ash filter cake is subsequently treated to recover the contained lithium carbonate.

3) The filtered melt is fed into the reducer, and reacted with carbon. The melt temperature is raised from 450°C to ~850°C by heat from the combustion of part of the carbon with air, and the sulfite and sulfate in the melt are completely reduced to sulfide (M_2S).

4) The melt stream from the reducer is passed into a quench tank where its temperature is lowered from 850°C to 450°C by mixing with cooler melt and by passing through a heat exchanger. The effluent from the quench tank is filtered to remove unreacted coke and coke ash and then passed on to the regenerator.

5) In the regenerator, the reduced melt is reacted with carbon dioxide (produced in the reduction step) and steam in a multi-stage, countercurrent sieve-tray column. The sulfide in the melt is completely regenerated to carbonate (M_2CO_3), and the sulfur is released as hydrogen sulfide (H_2S). The hydrogen sulfide is passed to the Claus plant, where it is converted to elemental sulfur.

6) The regenerated melt is recirculated to the scrubber, with the small filter melt losses being made up by addition of fresh carbonate.

CHEMISTRY OF THE PROCESS

The alkali carbonate eutectic melt[1] used in the process is a mixture of 32 wt % lithium carbonate, 33 wt % sodium carbonate, and 35 wt % potassium carbonate. The physical properties of the eutectic are given in Table 1.

TABLE 1
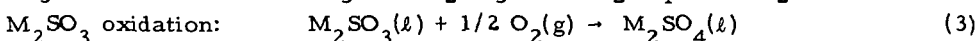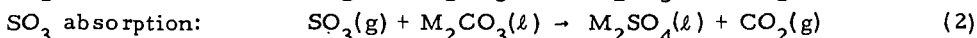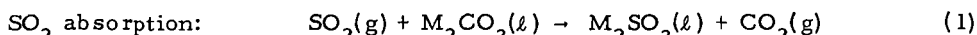
PHYSICAL PROPERTIES OF THE ALKALI CARBONATE EUTECTIC

Property	Magnitude	Reference
Melting Point	397°C	2
Molecular Weight	100 gm/mole	2
Heat of Fusion	6.6 kcal/gm-mole @ 397°C	2
Density	2.12 gm/cc @ 450°C	3
Viscosity	9.82 cp @ 450°C	4
Heat Capacity	40.39 cal/gm-mole @ 450°C	2
Surface Tension	236.9 dynes/cm @ 450°C	3

The melt has several chemical and physical properties which offer advantages for scrubbing sulfur dioxide from flue gas. It is a liquid which is easy to handle, pump and transport, and has a negligible vapor pressure so that it is not lost by evaporation and does not require high-pressure equipment. It is a strong base; therefore it reacts rapidly with acidic sulfur oxides, so that scrubbing contact time can be short. Since the entire liquid is a strong base, it has a high capacity for sulfur oxides and the amount of melt which must be regenerated continuously is relatively small. The great affinity of the melt for sulfur oxides leads to the removal of large percentages of the sulfur oxides from even very dilute gas streams. The use of this melt in the scrubber at 450°C does not cool off the gas stream or saturate it with water vapor. Finally, the carbonate will react with other acidic gaseous pollutants such as NO_2 and HCl; therefore the potential exists for control of other pollutants such as NO_x by the same process.

The chemistry of each step of the process has been studied in detail and is summarized below.

1. The Scrubbing Step
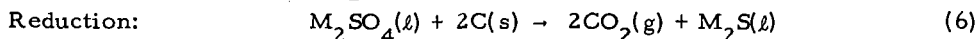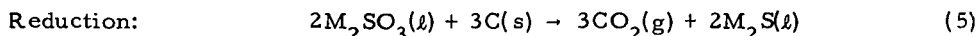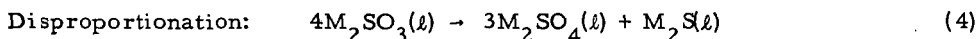
The reactions taking place in the scrubber are

SO$_2$ absorption: $\quad\quad$ $SO_2(g) + M_2CO_3(\ell) \rightarrow M_2SO_3(\ell) + CO_2(g)$ $\quad\quad$ (1)

SO$_3$ absorption: $\quad\quad$ $SO_3(g) + M_2CO_3(\ell) \rightarrow M_2SO_4(\ell) + CO_2(g)$ $\quad\quad$ (2)

M$_2$SO$_3$ oxidation: $\quad\quad$ $M_2SO_3(\ell) + 1/2\,O_2(g) \rightarrow M_2SO_4(\ell)$ $\quad\quad$ (3)

Absorption of SO_2 and SO_3 (Eq 1 and 2) is very rapid. For example in the laboratory when pure SO_2 is bubbled through 2 in. of melt, no odor of SO_2 can be detected in the exit gas (CO_2). The presence of O_2, CO_2, N_2, H_2O and fly ash does not affect the SO_2 removal. Melt which was regenerated 3 times in a series of cyclic tests was equally effective in removing SO_2. These results are not surprising in view of acid-base considerations in which the acidic SO_2 is neutralized by the basic alkali carbonate melt.

In an actual plant good contact must be made between the large volumes of flue gas and the relatively small melt stream. However, power plant integration requirements make it important to impose as small a pressure drop as possible on the gas stream. Because of this, a spray contactor has been selected as the molten salt scrubber concept. The spray contactor utilizes spray nozzles to break the melt up into small droplets for good gas-liquid contact, and a very efficient mist eliminator to prevent the gas stream from carrying melt mist out of the scrubber.

For example, in bench scale tests where hot synthetic flue gas was forced past a single melt spray nozzle at 25 ft/sec, sulfur oxide removal efficiencies of 97-100% were obtained and little (if any) melt in the exit gas could be found. The oxidation of M_2SO_3 (Eq 3) does not appear to be very rapid at the scrubber temperature. For example, when synthetic flue gas containing 1 vol % O_2 and 0.1 vol % SO_2 was bubbled through molten carbonate eutectic at 450°C, only 18, 31, and 44 wt % of the sulfite, formed from the absorbed sulfur dioxide, was oxidized to sulfate in 4, 7, and 14 hours, respectively. When the synthetic flue gas contained 5 vol % O_2 and 0.3 vol % SO_2, 42, 49, and 55 wt % of the absorbed sulfur oxide was oxidized to sulfate at similar times. Neither water nor fly ash had any appreciable effect on the oxidation rate.

2. The Reduction Step

The principal reactions occurring in the reduction step are disporportionation (Eq 4) and reduction (Eq 5 and 6).

Disproportionation: $\quad\quad$ $4M_2SO_3(\ell) \rightarrow 3M_2SO_4(\ell) + M_2S(\ell)$ $\quad\quad$ (4)

Reduction: $\quad\quad$ $2M_2SO_3(\ell) + 3C(s) \rightarrow 3CO_2(g) + 2M_2S(\ell)$ $\quad\quad$ (5)

Reduction: $\quad\quad$ $M_2SO_4(\ell) + 2C(s) \rightarrow 2CO_2(g) + M_2S(\ell)$ $\quad\quad$ (6)

The disproportionation rate of sulfite to form sulfide and sulfate (Eq 4) has been measured. Rate measurements indicate that disproportionation is a first order reaction which is not important at scrubber temperature (450°C) but is rapid at reduction temperatures (850°C). Therefore, in the process the major sulfur compound undergoing reduction is sulfate.
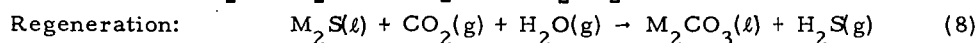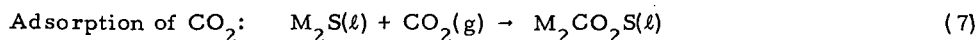
The sulfate (Eq 6) and sulfite (Eq 5) can be reduced by numerous substances. Fluidized coke is particularly good for this application since it is relatively inexpensive and has a low ash content. The reaction rate increased by about 2-3 for

each 50°C temperature rise; reduction times of 170, 30, 15, and 4 min were observed at 700, 800, 875, and 950°C, respectively. Therefore, the reduction reaction is carried out at temperatures of about 850°C or above.

In order to raise the temperature from 450°C to about 850°C and to supply the endothermal heat of reduction ($\sim$40 kcal/mole) considerable heat must be supplied. Because of materials limitations at this high temperature, the most feasible way to supply the heat of reaction is to generate the heat internally, by the combustion of carbon with air. This eliminates the need for heat transfer surfaces operating at high temperatures in a corrosive environment.

3. The Regeneration Reaction

Two important reactions occur in the regenerator: adsorption of carbon dioxide (Eq 7) and regeneration of carbonate (Eq 8).

Adsorption of CO_2: $\quad M_2S(\ell) + CO_2(g) \rightarrow M_2CO_2S(\ell)$ $\hfill$ (7)

Regeneration: $\quad M_2S(\ell) + CO_2(g) + H_2O(g) \rightarrow M_2CO_3(\ell) + H_2S(g)$ $\hfill$ (8)

Carbon dioxide is readily absorbed by molten melts containing sulfide. The amount of carbon dioxide absorbed increases as the temperature decreases and as the carbon dioxide partial pressure increases. Although the thiocarbonate intermediates (M_2CO_2S, M_2COS_2 and M_2CS_3) have not been identified in the melts, the chemistry involved indicates that the formation of these substances is the most likely explanation for carbon dioxide absorption. These intermediates are quite stable at temperatures of about 450°C and even appear to exist to some extent at temperatures as high as 950°C. Depending on the carbon dioxide partial pressure, about 0.5 to 1.5 moles of CO_2 are absorbed per mole of sulfide at 450°C. These absorption reactions are exothermic (15-20 kcal/mole) and are reversible.

Both carbon dioxide and steam must be reacted with the melt before regeneration occurs (Eq 8), although a substantial amount of carbon dioxide must be absorbed (Eq 7) before any evolution of hydrogen sulfide begins. However, since the intermediate has not been identified, the overall regeneration reaction is given in Eq 8. This reaction is rapid and complete, particularly at temperatures of about 450°C. Since the regeneration reaction is exothermic, the melt must be cooled during regeneration in order to maintain optimum regeneration temperatures ($450-500^{\circ}$C). The concentrated hydrogen sulfide stream evolved from the regenerator is fed to a Claus plant for conversion to sulfur.

4. Lithium Recovery

The melt used in this process is relatively inexpensive except for the lithium carbonate, therefore it is desirable to recover the lithium from the process filter cakes. An aqueous process has been developed for this purpose. The filter cakes are slurried with water and filtered to extract the very soluble sodium and potassium carbonates; lithium carbonate remains with the ash since it is relatively insoluble under these conditions. The ash-lithium carbonate cake is slurried in water and the lithium is solubilized by conversion to the bicarbonate. The ash is removed by filtration and the soluble bicarbonate in the filtrate is precipitated as the carbonate. The lithium carbonate is separated by filtration and returned to the process stream; the saturated lithium carbonate filtrate is recycled to conserve lithium. Laboratory tests have demonstrated that over 90% of the lithium can be recovered by this technique.

5. Materials and Components

A test program to select materials of construction which resist corrosion by the process melts has been underway for over 5 years. At first, all of the common metals, alloys, and ceramics were given screening tests. Successful candidates were then subjected to long-term tests, including one-year tests in rotating capsules. As a result, it was found that 300 series stainless steel was the best of the conventional alloys for service below 550°C, and that high density alumina was very corrosion-resistant even at 950°C.

After the preliminary selection of 300 series stainless steel, this alloy was subjected to further tests to study the effect of stress in the presence of chloride, oxygen, and water vapor, the effect of sensitization, and the rate at which the alloy constituents are leached out and transported under the influence of a temperature gradient. A molten salt loop has been in operation for several months as a part of these tests. The results indicated Type 304 and 347 stainless steel as the best of the conventional alloys for service below 550°C. High density alumina was very corrosion-resistant even at 950°C, therefore alumina bricks will be used to line the pilot plant reducer vessel.

The success of the type 300 series stainless steel in molten carbonates is due to the protective $LiCrO_2$ film which forms a compact, tenacious and self-healing layer. This film forms in about 500 hours and decreases the corrosion rate to a few mils per year. It has been shown that this film is essentially chromium oxide, with the vacant interstices filled with lithium. Lithium is the only stable ionic species present in the melt which is capable of filling the vacant interstice without expanding the oxide lattice.[5] Thus a stable diffusion barrier is formed which limits further corrosion.

ECONOMICAL EVALUATION OF THE PROCESS

An economic analysis of the process has been done to estimate the capital and operating costs of a large commercial plant. The economic analysis was made for a plant treating the gas stream from an 800 Mw generating station, operating at a 70% plant factor and burning coal containing 3% sulfur. A penalty charge for the high-temperature electrostatic precipitator was assessed. The cost of the Claus sulfur plant was also included. The total capital requirement is about $15 million, or $18.70 per kilowatt of generating capacity. This cost appears to be quite competitive with that for any other stack gas treatment process which recovers the sulfur in useful form.

The estimated annual operating cost for the 800 Mw plant assuming capital charges of 14% per year is 0.87 mills/kwh, without any credit being taken for the by-product sulfur produced. A return of $20/long ton for the sulfur is equivalent to a credit of 0.18 mills/kwh, reducing the operating costs to about 0.7 mills/kwh. This compares quite well with present estimates of 0.7 to 1.4 mills/kwh for low-sulfur or desulfurized fuels.

A thorough engineering and economic evaluation of the Molten Carbonate Process has recently been completed by Singmaster and Breyer, under contract to EPA.[6] For the same plant situation, their cost estimates were $16.81/kw for the capital investment (not including the Claus plant) and 0.95 mills/kwh for operating costs without by-product credit. The differences between the two estimates are probably well within the accuracy of the calculations.

PILOT PLANT PROGRAM

The pilot plant, funded by Consolidated Edison, Northeast Utilities, and North American Rockwell, will process a side stream of stack gases from a 335 Mw boiler at the Consolidated Edison Arthur Kill Station on Staten Island. It is planned to vary the SO_2 concentration at the inlet to the scrubber in order to map process performance over a wide range of conditions. The side stream will correspond to approximately 10 Mw equivalent of gas.

The gases, at $125^\circ C$, will be heated to about $450^\circ C$ by an in-line burner firing the same fuel as the boiler. The flue gases produced by the boiler when burning the fuel oil presently specified will contain ~ 200 ppm sulfur oxides. This concentration is low when compared to the 2000 ppm typical of gases produced by boilers burning coal containing 3% sulfur. In order to provide the flexibility needed to operate over a range of sulfur oxide concentrations, the pilot plant will be designed to recycle some sulfur dioxide from its Claus plant.

Construction of the pilot plant is underway. Plant start-up is scheduled in January, 1973. A one-year test program is contemplated. During this period of time all system and component performance tests and optimization studies can be completed.

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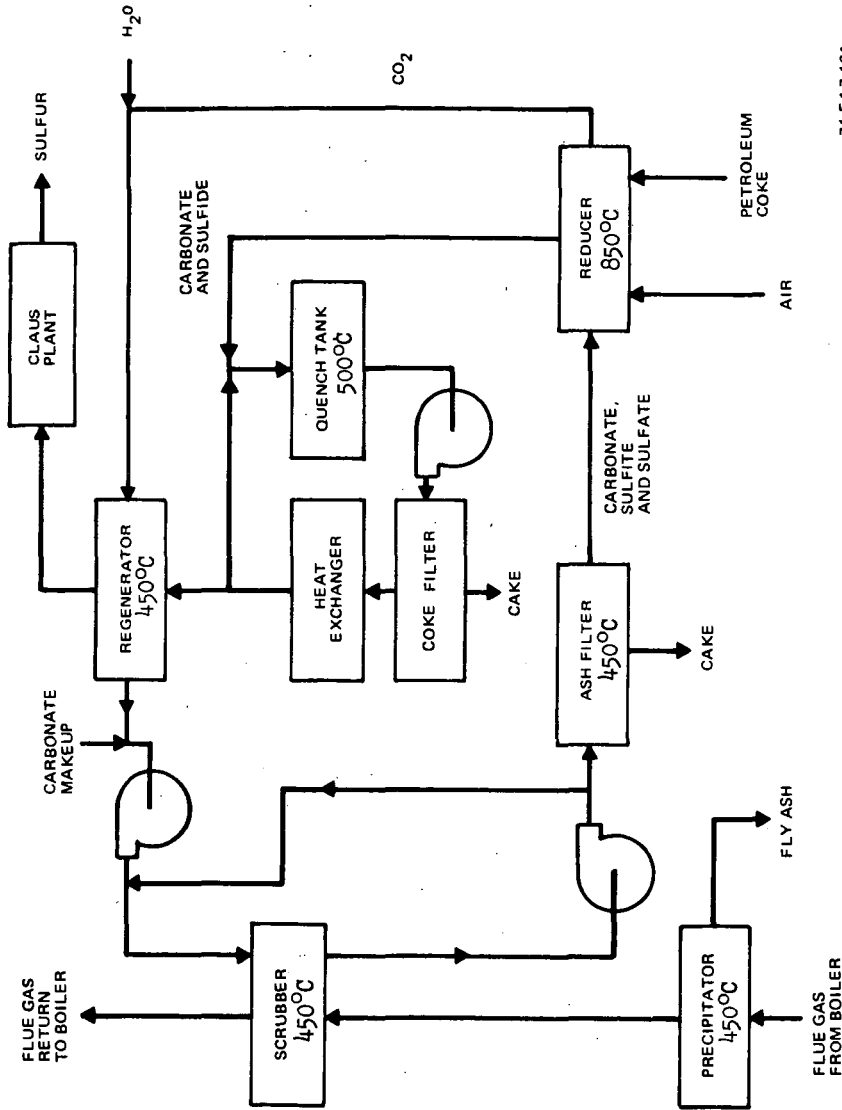
Figure 1. Molten Carbonate Process Flow Diagram